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GLASSY COATINGS FOR SINGLE-FIRING PRODUCTION OF CERAMIC FACING TILE

Yu. G. Pavlyukevich¹ and S. K. Machuchko¹

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Fritted glazes for single-firing ceramic facing tiles have been obtained in the system $R_2O-RO-Al_2O_3-B_2O_3-SiO_2$ (where $R_2O = Na_2O, K_2O$; $RO = CaO, ZnO, MgO, BaO$). The high molar content of calcium oxide (12.5 – 17.5%) in the glaze glasses shifts the formation temperature of the coatings to high values (1060 – 1100°C) and ensures that the degassing process in the ceramic paste is matched with the fusing process in the glaze.

Key words: facing tile, glaze, single firing, viscosity, melting temperature, linear thermal expansion coefficient, luster, surface defects.

The single-firing technology is widely used by the leading global manufacturers of ceramic tile for interior wall cladding. Compared with the conventional double-firing technology it makes it possible to reduce the consumption of fuel-energy resources per unit product (about 30%), reduce the total firing time for articles, use the production platforms in technological cycle more efficiently and increase production with the existing production resources [1].

In the double-firing technology the glaze is applied on a pre-fired ceramic tile and the glaze coating is formed mainly during the subsequent firing. In the single-firing process the entire tile production process is conducted in one heat-treatment cycle with the gas-release and phase-formation processes in the ceramic base proceeding in parallel with the glaze formation processes. The glaze mixes currently used in Belarus cannot be used in the single-firing technology for producing facing tiles, because these mixes are characterized by low sintering and softening temperatures and do not yield high-quality coatings.

In Belarus the single-firing technology has been implemented only at Berezaostroimaterialy JSC, using imported glazes and frits. This enterprise uses local mineral resources as well as clay from the Lukoml' deposit, dolomite from the Ruba deposit, quartz sand from the Gomel' GOK (Integrated Mining and Mineral Processing Combine), granite screenings from the Mikashevichi Unitary Enterprise Granit as well as imported raw material (DNPK clay from the Novoraiskoe deposit in Ukraine).

The present article is devoted to the development of mixes for transparent fritted glazes for facing tile produced by the single-firing technology.

The mixes for fritted transparent glazes were synthesized in the system $R_2O-RO-Al_2O_3-B_2O_3-SiO_2$ (where $R_2O = Na_2O, K_2O$; $RO = CaO, ZnO, MgO, BaO$) with the following contents, %²: SiO_2 54.5 – 67; B_2O_3 5 – 17.5; CaO 7.5 – 20; $Na_2O, K_2O, BaO, ZnO, MgO, Al_2O_3$ — remaining. The composition range of the synthesized glaze mixes is presented in Fig. 1.

The glaze glasses were melted in a gas-flame furnace at temperature $1450 \pm 20^\circ C$ and held at the maximum temperature for 1 h. The glazes were prepared by wet milling of frits with the addition of 8 wt.% kaolin and deposited by pouring onto a pre-wetted ceramic interior facing tile, which was chosen after the drying stage. The facing tile samples were fired in laboratory furnaces at temperatures 1050 – 1100°C as well as at temperatures $1100 \pm 10^\circ C$ at Keramin JSC and Berezaostroimaterialy JSC.

Several regions characterized by different coating quality were singled out in the experimental system. Lustrous defect-free coatings are formed in the temperature interval 1060 – 1100°C (see Fig. 1) with calcium oxide content 12.5 – 17.5% and barium oxide content 7.5 – 12.5%, which promotes good pouring and luster of the glaze. The thermal shock resistance of the coatings was 250°C, which shows that they are highly stable against sharp temperature differentials. The linear thermal expansion coefficient (CLTE) lies in the range $(65 - 69) \times 10^{-7} K^{-1}$.

¹ Belarus State Technological University, Minsk, Belarus (e-mail: keramika@bstu.unibel.by).

² Here and below, the molar content, unless stipulated otherwise.

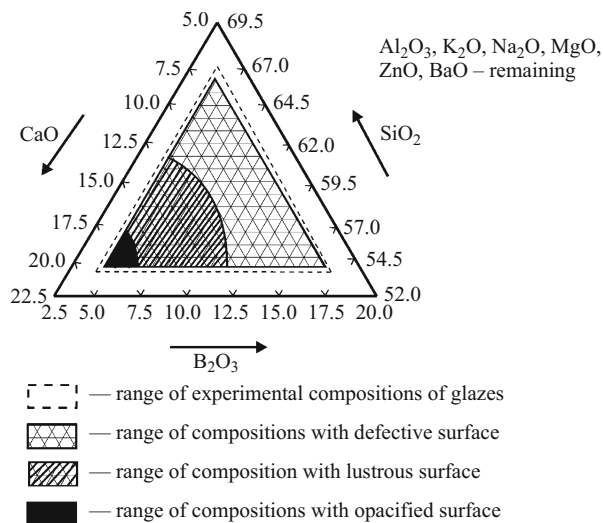


Fig. 1. Composition ranges of the synthesized glaze glasses (mol.%).

Compositions with 12.5–17.5 % B_2O_3 and 7.5–12.5% CaO are characterized by a large number of defects caused by foaming of the glaze. This is due to the low sintering and melting temperatures of these compositions, as a result of which the decarbonization process in the ceramic base is not matched with the fusing process in the glaze.

As the calcium oxide content increases from 17.5 to 20% the coatings undergo opacification due to the formation of new crystalline phases, specifically, wollastonite and pseudo-wollastonite.

To evaluate the technological properties of the coatings an MNO-2 heating microscope was used to determine the characteristic fusion points of the glazes (Fig. 2) for a cylinder pressed from the glaze powder. The sintering, softening and formation temperatures of spheres and hemispheres were determined.

The fusibility is characterized by the rate of softening of the glass and flow of the viscous melt along a solid surface at different temperatures. It is a complicated function of the viscosity, surface energy at the phase boundaries, crystallizability, crystallization onset temperature and density of the melt [2].

It was found that to obtain a defect-free coating the temperature interval between the softening point and the formation of a hemisphere must be 70–90°C and the softening temperature of the glaze must be shifted into the high-temperature range 1070–1080°C. This will promote greater completion of the gas-release processes occurring in the ceramic paste mainly at temperatures 920–1020°C and will make it possible to obtain articles with a high-quality glaze coating.

In evaluating the rheological properties of the glaze glasses it was determined that in the melting temperature range the character of the change in the viscosity must be conducive for rapid setting of the coating. As articles cool

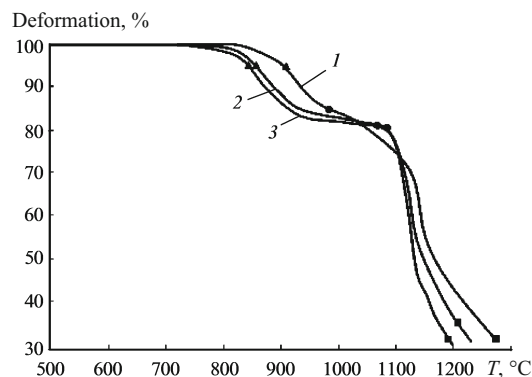


Fig. 2. Fusibility curves of the glazes: ▲) sintering; ●) softening; ■) melting; 1) glaze for double firing; glaze for single firing; 2) CaO content 7.5%; 3) CaO content 17.5%.

during the sintering process the remaining products of degasification are blocked in the ceramic–glaze boundary layer as a result of the sharp increase in the viscosity of the glaze glasses, which contain a high content of calcium oxide (12.5–17.5%).

Since the viscosity of the glasses is closely related with the structure, IR spectroscopy was used to study the changes occurring in the glasses (Fig. 3).

Distinct wide absorption bands peaking at 1385–1387, 1010–1027 and 464–466 cm^{-1} as well as weaker bands in the regions 708–798 and 1255–1272 cm^{-1} are present in the IR spectra.

The presence of absorption bands in the region 980–1040 cm^{-1} indicates the presence of silicon-oxygen groupings with different degrees of polymerization of the silicon-oxygen tetrahedra.

The shift of the main absorption band into the low-frequency part of the spectrum of the glasses from 1027 to 1010 cm^{-1} could be a consequence of a reduction of the degree of polarization of groupings comprised of the tetrahedra $[SiO_4]$, a transition from framework to layered and chain structures and an increase in the degree of differentiation by type of structural complexes.

The quite wide absorption band at 1387–1385 cm^{-1} in the high-frequency region of the spectrum 1350–1450 cm^{-1} is due to the vibrations of triply coordinated boron in complexes with polymerized groups $[BO_3]$, while for compounds with isolated $[BO_3]$ groups it is located in the region 1200–1300 cm^{-1} . The absorption band in the region 440–470 cm^{-1} corresponds to triply coordinated boron and reflects the out-of-plane deformation vibrations of the $B^{III}-O-B^{III}$ bonds. The presence of precisely these bonds in the glazes is confirmed by spectra in which the intensity of this band decreases with increasing CaO content and simultaneously the intensity of absorption in the region 1350–1450 cm^{-1} , corresponding to triply coordinated boron, decreases. This is a consequence of the fact that as the amount of oxygen introduced via CaO increases, the ratio of the groups $[BO_3]$ and $[BO_4]$ changes. The transition of boron

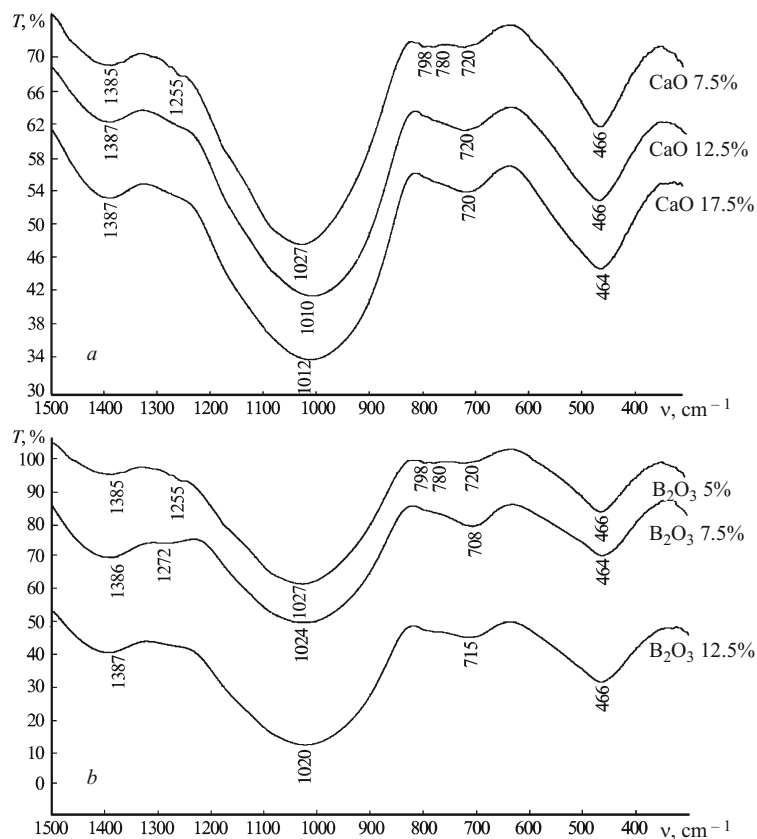


Fig. 3. IR spectra of the synthesized glasses: *a*) with constant molar content of B_2O_3 5%; *b*) with constant molar content of CaO 7.5%.

from its typical triple to quadruple coordination is due to the oxygen contributed by calcium oxide.

Calcium ions, acting as depolarizing cations, strongly influence the structure of the glasses, lowering the degree of polymerization of the main structural groupings. In the presence of calcium ions Si–O–Si bonds develop with Si–O nonbridging bonds, whose charge is saturated positively by the charged cation, being formed. However, the active influence of CaO on the structure of the glasses manifests not only in the degree of polymerization of the silicon-oxygen network but also in the coordination state of boron, as described above.

In summary, the quality and rheological characteristics of the glaze layer depend not only on the composition but also on the temperature-time conditions of firing. The main defects arising during single annealing of a facing tile are due to the mismatching between the degassing process in the ceramic base and the fusion process in the glaze. High calcium oxide content 12.5 – 17.5% in the glaze compositions shifts the formation temperature of the coatings into the high-temperature region 1060 – 1100°C and ensures that the formation process for the glaze coating is matched with the formation process in the ceramic base. The character of the change in the viscosity of the glaze as the ceramic tiles cool during single firing ensures rapid hardening of the glaze layer, creating conditions conducive for the formation of a high-quality defect-free coating [1].

The optimal compositions of the transparent coatings in the experimental system lie in the low-boron region with boron oxide content to 10%, which has its own limit as a result of the increase of the melting interval and saturation of the layer of glaze glass by the gas phase, resulting in defects ('pinholes') on the coatings. A low content of alkali-metal oxides to 6% together with B_2O_3 and Al_2O_3 determines the low linear thermal expansion coefficient and high thermal shock resistance of the coating. The optimal compositions characterized by CLTE in the range $(65 - 69) \times 10^{-7} \text{ K}^{-1}$.

The composition developed with CaO and B_2O_3 in amounts 12.5 and 7.5%, respectively, were tested at Bereza-stroimaterialy JSC and can be recommended for adoption in other enterprises in the construction materials industry that produce ceramic tiles for interior wall facing.

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